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14. ABSTRACT

Funding was provided by the Air Force Office of Scientific Research in order to support exploratory experiments for probing the tribological behavior of nano-coatings on real surfaces. Recent experiments have shown desirable tribological properties for these materials. However, most of these experiments are performed on coated surfaces which are not used in the real life application. We explored the tribological properties of these solid-liquid-solid systems by the triborheometry fixture that can be utilized with a commercial torsional rheometer in orderto explore the coupled rheological and tribological properties of complex fluids and solid-liquid systems. Using this new triborheometer fixture it is possible to obtain tribological information over a wider range of sliding velocities than is typically possible using conventional devices such as pin-and-disk systems. We seek to expand the detailed understanding of tribological systems when nano-coating is used on real surfaces. In particular, generating Stribeck curves provides a road map for the designer of such systems for a range of velocities, temperatures and other environmental factors. The outcome of

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A Executive summary

The overall objective of this research program was to investigate and quantify the impact of novel coating structures deposited on working surfaces on the tribological behavior of these systems through a set of exploratory experiments . To date, these surfaces are being tested using conventional techniques such as pin-and-disk or ball-on-disk systems while using substrates such as rigid quartz or Mica. It is acknowledged that tribotests on real engineering surfaces matter but few detailed studies have characterized the extent of these systems. To address this issue, we studied the tribological characteristics of nano-coated engineering surfaces. In addition, the effect of micro-particles in the rheology of these systems was investigated. Depends on the volume fraction of these particles in the liquid, their impact on the rheological and tribological properties of systems varies drastically.

We developed a new triborheometry fixture that can be utilized with a torsional rheometer to measure the frictional properties of a solid-fluid-solid system as well as a solid-solid pair as the sample gap and applied load are varied. The instrument enables a wide range of rotation rates to be imposed, and by varying the contact area of the lower fixture, a wide range of normal stresses can also be attained. The results can be represented in the form of a conventional Stribeck curve, or in terms of a more general 'friction map' of the gap- and load- dependent effective viscosity of the fluid. By utilizing the tribo-rheometer, our research benefits from several unique features that are essential to our approach. We take advantage of this system for controlling the temperature and relative humidity of the test section which are already built into the system for rheology pruposes.

We were able to show that polymer brushes grafted on solid surfaces do not reduce the friction coefficient but the wear of solid surfaces is drastically reduced due to the protection provided by the nano-structures.

In addition we performed the first set of rheological experiments on slurry of micro-particles in ionic liquids as a function of volume fraction and temperature. The non-Newtonian behavior of these systems is similar to other slurries but the effect of temperature and relative humidity need to be explore in detail. The rheology of the dry particles were also tested for comparison. During these experiments we discover the behavior of the granular particles are very similar to materials going through glass transition. This discovery is published in Nature Physics journal [1].

B Research Effort

Conventional cone-plate or parallel-plate rheometers and tribological devices such as pin-on-disk testers have a number of common design characteristics. In particular, they typically utilize torsional flows to constrain and contain the test fluid, allow the attachment of different test geometries and, finally, incorporate electromechanical subsystems with wide dynamic ranges in order to impose and/or measure known rotation rates, normal loads and torques on fluid samples. It is thus plausible to consider the design of a new test fixture that can generate both rheological and tribological data. We design a self-centering and self-leveling *tribo-rheometry* fixture which can be used in conjunction with a standard torsional rheometer. The sample dimension H can be smoothly varied from values characteristic of standard rheometry down to values less than the characteristic roughness of the fixtures (i.e. to nominally a 'zero-gap' separation) under conditions of controlled normal load. The resulting test data can be used to generate the familiar Stribeck diagrams and traditional rheograms as well as to extend the friction map ideas of Luengo and coworkers [2, 3] and Yamada [4] to systems involving more rheologically-complex macromolecular or multiphase fluids and hard or soft bounding surfaces which are not atomistically smooth.

B.1 Experimental Setup

Triborheometer Design & Geometry The tribo-rheometer [5] is a fixture that can be added to a commercial torsional rheometer to capture the tribological properties of the system (i.e. the frictional interactions of a fluid-surface pair) as well as the 'bulk' rheological properties of the fluid under shear. We used a torsional rheometer (AR-2000, TA Instruments Inc.) with a stainless steel parallel plate configuration as shown in figure 1. Due to the radial variation of the local shear stress τ in the parallel plate geometry, the cone and plate geometry is more suitable for traditional rheological measurements of complex fluids. The advantage of the parallel plate geometry is the ability to readily vary the gap size, H, as compared to the fixed cone angle of a specified conical fixture. Decreasing the gap H enables higher shear rates to be attained for the same fluid which is not possible with a cone and plate system. The lower bounding surface is a Peltier plate assembly which is used not only to control the temperature of the fluid sample, but also to measure the normal force acting on the surface using a force transducer that is mounted below the surface.

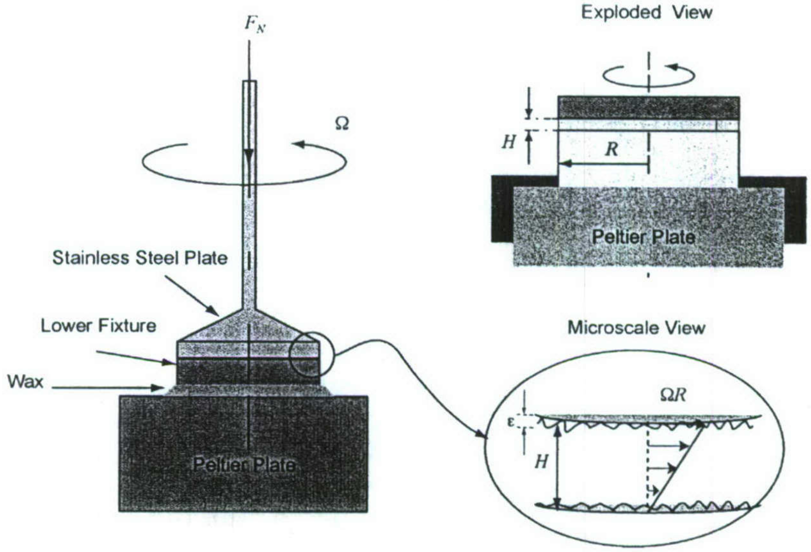

Figure 1: The schematic of the tribo-rheometer and its fixtures.

To obtain tribological properties using a torsional rheometer, a new *triborheometry* fixture is designed and installed on the surface of the Peltier plate. The simple design enables the user to interchange different hard or soft materials as the lower fixture in place of using the surface of the Peltier plate.

When a torque, T, is applied to the top plate, the fixture reaches a certain constant angular velocity, Ω, which is measured by an optical encoder on the shaft. Through a feedback system available in the AR-2000 rheometer, one can design a test procedure that then varies the angular velocity over several orders of magnitude at either constant gap or constant normal force and measures the corresponding torque required for a specified velocity.

The shear rate, $\dot{\gamma}$, in the fluid sample resulting from the rotating top plate is simply $\dot{\gamma} = \Omega r/H$. The applied torque is found by integrating the shear stress, τ, acting on the rotating surface of the plate [6].

For Newtonian fluids the torque is linearly related to the rim shear rate. The simple

relation between the applied torque, T, and the shear stress, τ_R, at the rim of the disk is

$$\tau_R = \frac{2}{\pi R^3}T. \tag{1}$$

The viscosity of the fluid is then obtained directly from the shear stress or measured torque $\eta = \tau_R/\dot{\gamma}_R = 2HT/(\pi\Omega R^4)$.

If the gap is progressively decreased, the two surfaces eventually begin to contact each other resulting in a steady increase in the positive normal force or thrust exerted. Using a feedback loop in the rheometer, this applied normal force can be set and held at a constant value with an accuracy of ± 0.1 N. When the normal force is set, by running a similar velocity sweep procedure, one can measure the torques and subsequently the variation in the rim shear stress $\tau_R(\Omega)$ with angular velocity can be obtained. This enables us to generate a Stribeck diagram for the fluid-solid pair. In non-rotating systems, the dimensionless number of choice is the Sommerfeld number which is defined as $So = \eta V/P$, where V is the linear velocity and P is the normal force per unit length of the contact. For rotating systems, the Gumbel number [7] is defined as:

$$Gu = \frac{\eta\Omega}{\sigma} = \frac{\eta\Omega\pi R^2}{F_N}. \tag{2}$$

where η is the shear viscosity, and $\sigma = F_N/\pi R^2$ is the average or nominal normal stress acting on the rotating plate. Knowing the preset normal force, the area of the plate, and fluid viscosity, the measured radial velocity can be converted to dimensionless values of the parameter Gu. The coefficient of friction, μ, is defined as the ratio of the shear stress, τ_R, to the normal stress, σ. By calculating the shear stress from the imposed torque using the stress factor for this geometry from equation(1), a Stribeck diagram can thus be generated.

Effect of surface roughness To explore the effect of surface roughness, we use fixtures made from three different materials. A roughened copper disk (ϵ = 678.7nm), a smooth copper disk (ϵ = 93.1nm), and a glass annulus machined from a $\lambda/20$ optical flat (ϵ = 0.7nm). The r.m.s surface roughness of these surfaces are measured using a contacting surface profiler (P10 Tencor Inc.). The applied normal force is set at $F_N = 10.0 \pm 1.0$N and the experimental results are shown in figure 2. At very low rotation rates, in the boundary lubrication region, the coefficient of friction is approximately constant in each experiment, with $\mu_{glass} < \mu_{copper}$. The differing roughness values of the two copper fixtures is irrelevant

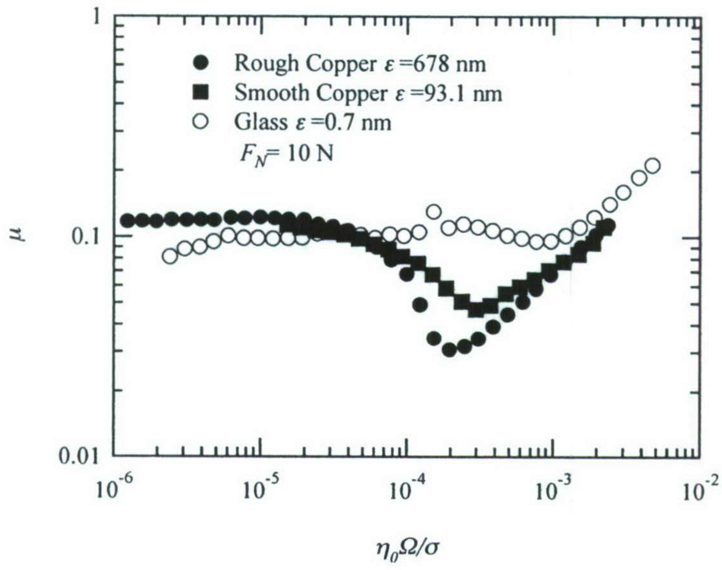

Figure 2: The effect of surface roughness on tribology is shown on a Stribeck diagram. Rough copper (•), smooth copper (■), and glass (○) are tested with Pennzoil 80W-90 lubricant and normal force of 10N.

in this regime since the upper and lower surfaces are in intimate contact in each case. At very high rotation rates, all three curves fall on a single line with slope of 1.0 characteristic of hydrodynamic lubrication. However, in the mixed lubrication regime, the coefficient of friction is a strong function of the surface roughness, and the maximum decrease in μ arises for the roughest surface. The crossover from mixed lubrication to hydrodynamic lubrication also occurs at increasingly high Gumbel number (or shear rate) as the r.m.s roughness decreases.

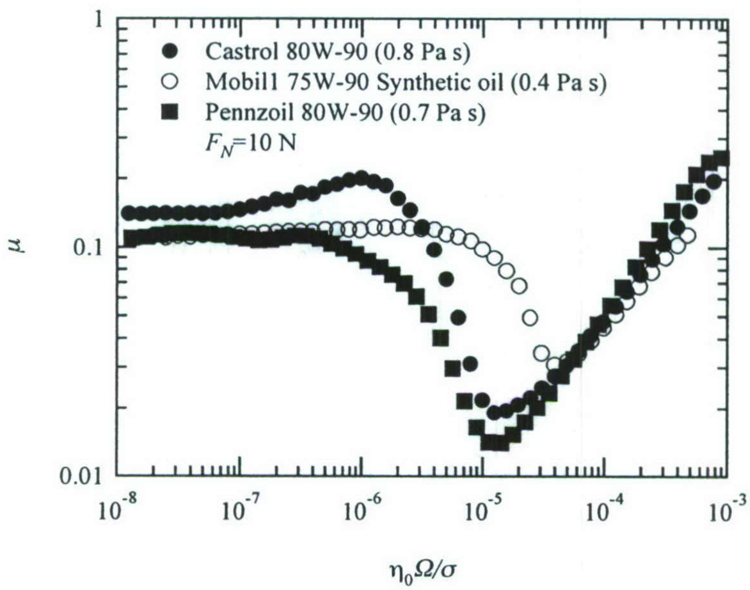

Figure 3: The effect of lubricant fluid on tribology is shown on a Stribeck diagram. Castrol 80W-90 (•),Mobil1 75W-90 synthetic oil (○), and Pennzoil 80W-90 (■) are tested on a copper fixture with normal force of 10N.

C Accomplished work

C.1 Effect of grafted polymers on tribological properties

Grafting polymers onto surfaces is often used to modify surface forces and has important applications in many areas. In the last 15 years, there have been a large number of experimental and numerical simulations on the properties polymer brushes. The static properties of polymer brushes are very well understood. Klein and co-workers [8–12] have done the majority of experimental work on polymer brushes. In a review article, Grest [13] summaries the effect of normal and shear forces on polymer brush. It has been shown that polymer brush can reduce the friction forces drastically. However, most of the experiments have been performed on ideal systems with Mica surfaces on very small areas. There is a certain need to further explore the application of polymer brushes on more complicated and larger surfaces. Our preliminary results of using polymer brush on metallic surfaces are shown in figure 4. The AFM (Atomic Forced Microscopy) tests show the silicon surface is well-protected by the polymer brush layer (polyvinylalcohol) against wear, due to friction.

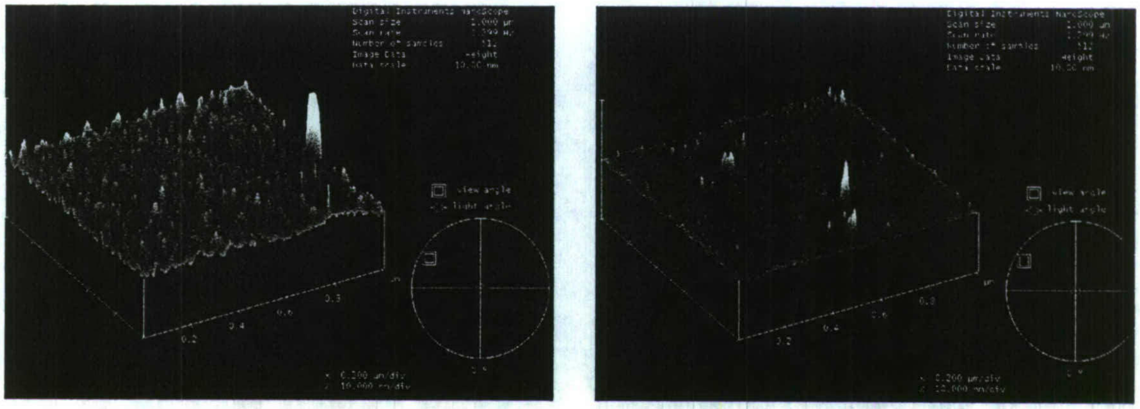

Figure 4: The topology of a silicon wafer covered with polymer brush (polyvinylalcohol) using AFM (a) before and (b) after a tribology test.

The smart nano-composite coatings with "chameleon" surface adaptation are nano-structures which self-adjust to surrounding conditions such as temperature and relative humidity. This type of behavior is very important for many applications. Researchers at the Air Force research laboratory [14–17] have shown the importance of these coatings for satellite and other space-born applications because of their performance over a range of temperatures and harsh conditions.

Having access to the state-of-the-art facilities in micro- and nano-fabrication at UCLA allows us to create a variety of modified surfaces. Polymer brushes will be deposited on designated surfaces through the laboratory of the resident expert, Prof. Y. Cohen, of the Department of Chemical Engineering.

Using this system, we can characterize many types of microscopic surface structures and their effects in friction of surfaces. In figure 5, our results represent the effect of polymer brush in friction. The Stribeck curve of silicon-silcon surfaces with a glycerol-water mixture (70%-30%), is compared with a similar system with grafted polymer brush (polyvinylalcohol). The reduction of the coefficient of friction and elimination of the mixed region is due to the effect of polymer brush.

The effect of polymer brush on different solid-liquid-solid system will be investigated by performing triborhelogical experiments, as explained previously. Stribeck diagrams will then be generated to help understand of these results. These results will then be compared with the tribological results of the same systems without polymer brush. A number of

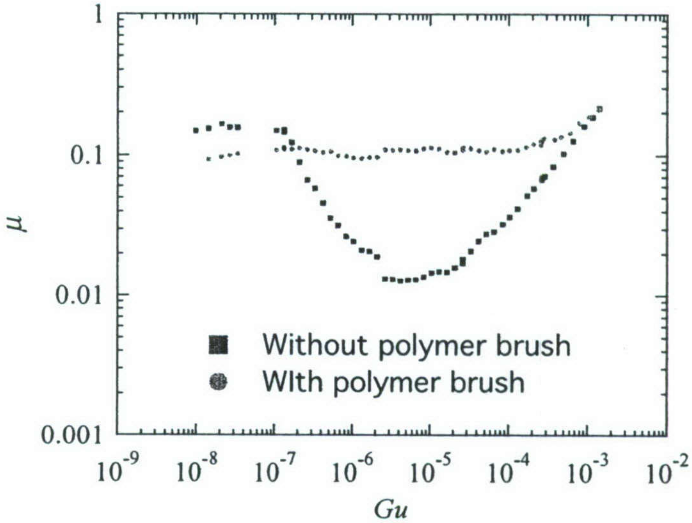

Figure 5: Stribeck curves for preliminary results of silicon surfaces with (•) and without (■) grafted polymer brush. The lubricant is a glycerol-water mixture (70%-30%). Polymer brush reduced the coefficient of friction in the boundary lubrication regime and eliminated the mixed region as expected.

lubricants and surface materials will be used in this research.

C.2 Effect of micro-particles in rheological and tribological properties

For the first time, we are able to study rheological and tribological properties of solid/liquid/solid systems of ionic liquids suspensions on a controlled environment. Our test liquid is a Di-akylimidazolium based ionic liquids with the bis(trifluoromethanesulfonyl)imide (TFSI- = N(SO2CF3)2-) anion (Im10RTFSI). We used silicon microspheres (R=50 um) to produce the suspensions with desired concentrations (mass based). The rheological results for three different liquids: 0%, pure liquid; 10%, dilute solution; and 50%, slurry are shown in this figure. These experiments are performed at dry environment (nitrogen 99.99% atmosphere) for three temperatures (5 C, 25 C and 75 C). At the lower concentrations of the particles, the addition of the particles do not change the rheological behavior of the liquid and the change in viscosity follows the Einstein relation for dilute systems. For the slurry system, the liquid viscosity behave as a non-Newtonian liquid and it follows the modified Cross model meaning liquids has a yield stress. The low shear viscosity of these fluids varies with

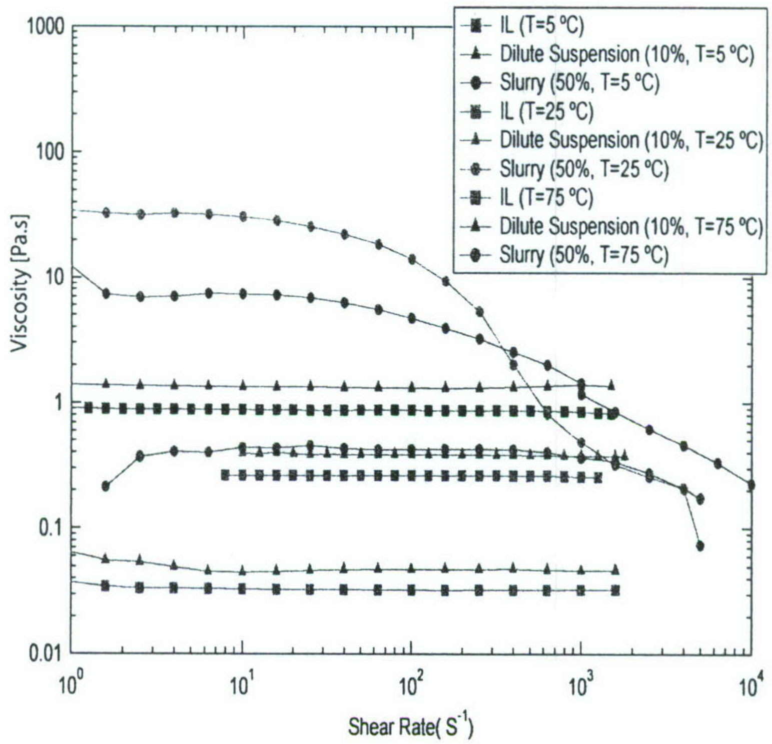

Figure 6: Effect of volume fraction and temperature on the rheological behavior of slurries of ionic liquids.

temperature and it follows an Arrhenius behavior as expected ($viscosity \sim exp(1/temp)$) as shown in figure 6.

We have also studied the rheological properties of dry particles. Since we tested our system for variation of mass fractions of liquid and particles, the rheology of the dry particles were also tested for comparison. During these experiments we discover the behavior of the granular particles are very similar to materials going through glass transition as shown in figure 7. This discovery is accepted for publication at Nature Physics [1].

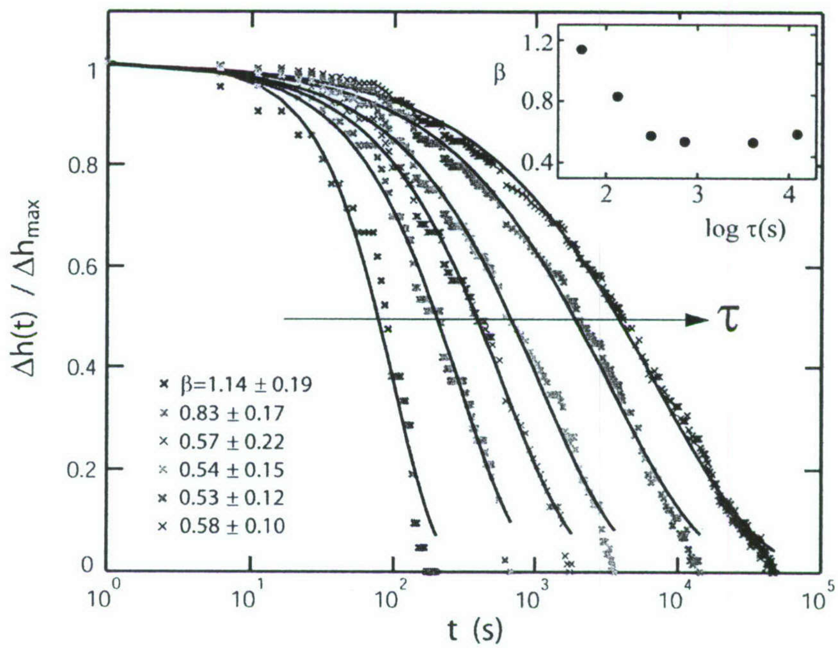

Figure 7: A semi-log plot of structural aging of sheared granular mixture. The non-Arrhenius and the non-exponential relaxations are reminiscent of the key features of glassy liquids (From Lu et al. [1]).

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